

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 845 526 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
03.06.1998 Bulletin 1998/23

(51) Int. Cl.⁶: **C11D 3/39**, C11D 3/36,
C11D 3/20, C11D 3/28
// C11D1/66, C11D1/88

(21) Application number: **97203428.4**

(22) Date of filing: **05.11.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• **Jadesjö, Gunilla**
442 33 Kungälv (SE)
• **Jönsson, Gunnil**
449 90 Nol (SE)

(30) Priority: **29.11.1996 SE 9604413**

(74) Representative:
Jönsson, Christer
Eka Chemicals AB,
Patent Department,
Box 11556
100 61 Stockholm (SE)

(71) Applicant: **Eka Chemicals AB**
445 80 Bohus (SE)

(54) **Cleaning, disinfecting and bleaching composition**

(57) The invention relates to a composition suitable for cleaning, disinfection and bleaching comprising an acidic aqueous solution of hydrogen peroxide, a surfactant, a phosphonic acid based complexing agent and citric acid. The invention also relates to use of such a composition for disinfection, bleaching, removal of stains from textiles, or removal of lime deposits.

EP 0 845 526 A2

Description

The present invention relates to an acidic aqueous composition suitable for cleaning, disinfection and/or bleaching comprising hydrogen peroxide, as well as use of such a composition.

Hard surface cleaning and disinfection, laundry bleaching and stain-removal, domestic as well as industrial, is often performed with chlorine based chemicals such as hypochlorite in aqueous solution which generally is effective for disinfection and bleaching, or organic solvents, enzymes and surfactants effective for stain-removal. However, hypochlorite is not useful for removing lime soap and it may also damage textile fibres and the original colours thereof. Further, for environmental reasons it is desirable to avoid chlorine based cleaning agents.

Hydrogen peroxide is known as an environmental friendly oxidiser and disinfectant, but to be efficient a rather high concentration and/or a long contact time is necessary. In the bacterial cell hydrogen peroxide reacts with -SH groups and thereby destroys SH containing enzymes and inhibit the protein synthesis. However, hydrogen peroxide has a poor storage stability, particularly in combination with other ingredients such as surfactants or organic acid. Although the hydrogen peroxide stability can be improved by addition of chelating agents like phosphonates, it is hard to find a phosphonate that both is biodegradable and effective as a hydrogen peroxide stabiliser.

EP-B1-87049 discloses a composition for disinfection comprising hydrogen peroxide, an acidic phosphorous compound such as phosphoric acid, and a complexing agent selected from certain phosphonic acids or salts thereof.

EP-A1-517996 discloses a hydrogen peroxide based bleaching composition comprising a specific class of surfactants.

WPI Acc. No 93-004727/01, abstract of JP-A-4332800 discloses a detergent composition comprising hydrogen peroxide, an organic or inorganic acid, and a carboxylic acid type polymer.

WPI Acc. No 88-004846/01, abstract of JP-A-62270509 discloses a composition for removing marine creatures from constructions used in sea water, the composition comprising citric acid, hydrogen peroxide and a surfactant.

WO 93/14183 discloses a detergent composition comprising a surfactant, oxygen bleach such as hydrogen peroxide and a metal sequestering agent.

WO 91/08981 discloses a solution for stabilizing hydrogen peroxide comprising citric acid, tartaric acid and phosphoric acid.

WO 94/07803 discloses the use of a composition comprising an oxidising agent, an organic acid and a phosphonic acid for removing magnetite deposits in water supply systems.

It is an object of the present invention to provide a

storage stable composition based on hydrogen peroxide which is effective for several functions including cleaning, bleaching, disinfection, removal of stains on textiles and removal of lime deposits. It is another object of the invention to provide a composition only containing environmentally acceptable components. The composition according to the invention comprises an acidic aqueous solution of hydrogen peroxide, a surfactant, citric acid and a complexing agent based on phosphonic acid, dipicolinic acid or derivatives thereof. Suitably, the pH of the composition is below 4 preferably below 3, most preferably below 2, which improves the antimicrobial activity as well as the capability of removing lime deposits or lime soap in, for example, bath tubs, toilet bowls or the like. A low pH also improves the stability of the hydrogen peroxide. However, the pH preferably is above about 0.5, most preferably above about 1.

It has surprisingly been found that citric acid, unlike most environmental friendly acids, does not cause any substantial decomposition of the hydrogen peroxide in aqueous compositions also containing surfactants and phosphonic acid or dipicolinic acid based complexing agents. It is preferred that, apart from citric acid and phosphonic and/or dipicolinic acids or derivatives thereof, the composition does not contain any substantial amounts of other organic acids. From an environmental point of view it is also preferred that the composition does not comprise any substantial amounts of phosphoric acid or phosphates.

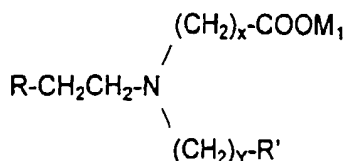
The surfactant facilitates removal of dirt and especially non-ionic surfactants are excellent on removing fat and pigments but they also enhance the antimicrobial effect as they destroy bacterial cell membranes. Preferred surfactants are compatible with hydrogen peroxide in acidic solutions which means that neither do they cause decomposition of the hydrogen peroxide, nor does the hydrogen peroxide or the acid cause decomposition of the surfactants. Further, the surfactants are preferably environmental friendly and biodegradable.

The composition contains one or several different surfactants. Preferably, it comprises a non-ionic surfactant or an amphoteric surfactant or a mixture thereof. Although not preferred, it is also possible to include anionic surfactants as an alternative or as a complement.

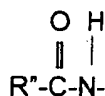
Preferred non-ionic surfactants are selected from ethoxylated fatty acids, alcohols, amines or amides, preferably comprising from 1 to 12 most preferably from 4 to 8 mols ethylene oxide per mol acid, alcohol, amine or amide. Preferably the acid, alcohol or amide comprises from 7 to 15, most preferably from 9 to 11 carbon atoms. Useful non-ionic surfactants can be high foaming such as an ethoxylated alcohol containing 11 carbon atoms and 8 ethylene oxides, or low foaming such as a narrow range ethoxylated alcohol containing 9 carbon atoms and 6 ethylene oxides.

Preferred amphoteric surfactants are selected from derivatives of preferably aliphatic amines comprising one or more anionic groups such as carboxy, sulfo, or

sulfato. Particularly preferred amphoteric surfactants satisfy the formula:



wherein x and y are, independently from each other, from 1 to 5, R' is -COOM₂ or -OH, M₁ and M₂ are, independently from each other, H, ammonium or an alkali metal such as Na, K or Li, R is a straight or a branched carbon chain having from 1 to 8 carbon atoms or an amide of the formula:

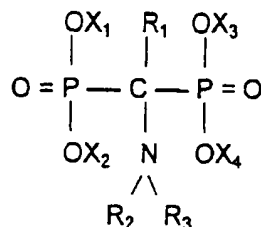


wherein R'' is a straight or a branched carbon chain having from 1 to 8 carbon atoms. It is preferred that R' is COOM₂ and that R is a straight or a branched carbon chain. Examples of preferred amphoteric surfactants are octylimino dipropionate and capryloampho diacetate which are commercially available under the trademarks Ampholak® YJH40 (Akzo Nobel) and Ampholak® XJO (Akzo Nobel), respectively.

At least one complexing agent based on phosphonic acid, dipicolinic acid or derivatives thereof should be included in order to obtain satisfactory storage stability of the hydrogen peroxide. One or several phosphonic acid based complexing agents is preferably present in an amount from about 0.5 wt% to about 10 wt%, most preferably from about 1 wt% to about 4 wt% based on the content of hydrogen peroxide. Dipicolinic acid or derivatives thereof may be present in an amount from about 0.25 to about 5 wt%, preferably from about 0.5 to about 2 wt% based on the content of hydrogen peroxide. The complexing agents also enhance the microbial effect since they chelate cat-ions like magnesium and calcium which have an important role in the bacterial cell. Examples of useful derivatives of dipicolinic acid are picolinic acid, acid, 2,6-pyridine dialdehyde or 2,2-dipyridyl amine. Examples of useful phosphonic acid based complexing agents are those that are commercially available such as 1-hydroxyethylidene-1,1-diphosphonic acid, 1-aminoethane-1,1-diphosphonic acid, aminotri (methylenephosphonic acid), ethylene diamine tetra (methylenephosphonic acid), hexamethylene diamine tetra (methylenephosphonic acid), diethylenetriamine penta (methylenephosphonic acid) and diethylenetriamine hexa (methylenephosphonic acid), as well as salts thereof. Particularly high stability can be achieved by including both a phosphonic acid and dipi-

colinic acid or a derivative thereof.

Preferred phosphonic acid based complexing agents are those that are at least partly biodegradable. Therefore, the composition preferably comprises a complexing agent selected from biodegradable 1-aminoalkane-1,1-diphosphonic acids, or salts thereof, preferably of the formula:



wherein R₁ is selected from hydrogen, C₁-C₄ alkyl and phenyl; R₂ and R₃, independently from each other, are selected from hydrogen, C₁-C₂₂ alkyl, C₅-C₆ cycloalkyl, phenyl, C₇-C₁₈ alkylphenyl, C₇-C₁₈ phenylalkyl, a C₁-C₁₀ alkanol radical, a carboxy alkyl radical having up to 10 carbon atoms, wherein R₂ and R₃ together with the nitrogen atom can form a piperidino, pyrrolidino or a morpholino group; and X₁ to X₄, independently from each other, are selected from hydrogen, alkali metal and ammonium. Preparation of such phosphonic acids are described in, for example, US 3899496, US 3979385 and "Synthesis of 1-dialkylaminoalkylidene diphosphonic acids and their properties for complex formation", Fukuda, M., et al, Yukagaku, Vol. 25, No. 6, pp. 362-64 (1976).

Preferably R₁ is hydrogen. It is also preferred that R₂ and R₃ are selected from hydrogen, C₁ to C₄ alkyl, or together with the nitrogen form a morpholino group. Particularly preferred complexing agent are selected from morpholinomethane diphosphonic acid, N,N-dimethyl aminodimethyl diphosphonic acid, aminomethyl diphosphonic acid, or salts thereof, preferably sodium salts.

A composition of the invention can be in the form of a concentrate intended to be diluted before use. Such a concentrate may suitably contain from about 10 wt% to about 60 wt%, preferably from about 30 wt% to about 50 wt% of hydrogen peroxide, from about 5 wt% to about 30 wt%, preferably from about 10 wt% to about 20 wt% of surfactants, from about 0.5 wt% to about 10 wt% preferably from about 1 wt% to about 5 wt% of citric acid, and from about 0.05 wt% to about 10 wt%, preferably from about 1 wt% to about 5 wt% of phosphonic acid based complexing agents, alternatively from about 0.025 to about 5 wt%, preferably from about 0.5 to about 2.5 wt% of dipicolinic acid or derivatives thereof. The balance is preferably mainly made up of water. The pH of the concentrate is suitably from about 0.5 to about 3, preferably from about 1 to about 2. Such a composition is preferably diluted from about 10 to about 50 times before use and is then particularly suitable for cleaning

and disinfection of hard surfaces, particularly in the food industry where it is important to destroy human pathogenic as well as product spoiling micro-organisms and spores.

A ready to use composition suitable for cleaning, disinfection or stain removal in households suitably contains from about 0.1 wt% to about 10 wt%, preferably from about 4 wt% to about 6 wt% of hydrogen peroxide, from about 0.1 wt% to about 10 wt%, preferably from about 2 wt% to about 6 wt% of surfactants, from about 0.1 wt% to about 3 wt% preferably from about 0.5 wt% to about 1 wt% of citric acid, and from about 0.01 wt% to about 5 wt%, preferably from about 0.1 wt% to about 1 wt% of phosphonic acid based complexing agents, alternatively from about 0.005 to about 2.5 wt%, preferably from about 0.05 to about 0.5 wt% of dipicolinic acid or derivatives thereof. The balance is preferably mainly made up of water. The pH of the composition is suitably from about 1 to about 4, preferably from about 2 to about 3. The composition is very effective for cleaning hard surfaces in kitchens and bathrooms and for removing stains from textiles. It can also be used outdoors for removing or inhibiting growth of mould or algae on wood or other materials. If appropriate, it can be combined with other cleaning agents or detergents, such as ordinary alkaline detergents for machine washing.

A composition of the invention can easily be prepared by simply mixing the components to desired concentrations.

The invention also relates to use of a composition as described herein for disinfection, bleaching, removal of stains from textiles, or removal of lime deposits.

The invention is further illustrated through the following examples which, however, are not intended to limit the scope of the invention. If not otherwise stated, all contents and percentages refer to % by weight.

Example 1: A composition according to the invention consisting of an aqueous solution of 5% of hydrogen peroxide, 5% of ethoxylated C₁₀-C₁₄ fatty alcohols with 7 mols ethylene oxide and 1 mol propylene oxide as a high foaming non-ionic surfactant, 0.2% of morpholinomethane diphosphonic acid disodium salt and 1% of citric acid was prepared by mixing the components. The pH was 2.3. The stability of the hydrogen peroxide was tested by storing the composition 42 days at 40°C. It was found that 95.9% of the hydrogen peroxide remained.

Example 2: A composition according to the invention consisting of an aqueous solution of 5% of hydrogen peroxide, 2.5% of ethoxylated C₁₀-C₁₄ fatty alcohols with 7 mols ethylene oxide and 1 mol propylene oxide as a high foaming non-ionic surfactant, 2.5% of ethoxylated C₁₆-C₁₈ amide with 4 mols ethylene oxide as a low foaming non-ionic surfactant, 0.2% of morpholinomethane diphosphonic acid disodium salt and 1% of citric acid was prepared

by mixing the components. The pH was 2.5. The stability of hydrogen peroxide was tested by storing the composition 42 days at 40°C. It was found that 96.6% of the hydrogen peroxide remained.

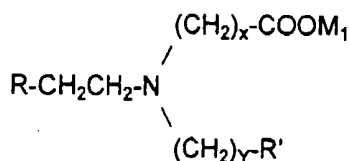
Example 3: A composition A according to the invention consisting of an aqueous solution of 4.9% of hydrogen peroxide, 50 g/l of ethoxylated C₁₀-C₁₄ fatty alcohols with 7 mols ethylene oxide and 1 mol propylene oxide as a high foaming non-ionic surfactant, 2 g/l of morpholinomethane diphosphonic acid disodium salt and 10 g/l of citric acid was prepared by mixing the components. The pH was 2.3. A composition B according to the invention was prepared in the same way with the exception that 1-hydroxyethylidene-1,1-diphosphonic acid was used instead of morpholinomethane diphosphonic acid which gave a pH of 1.8. The stability of the hydrogen peroxide was tested by storing the compositions 830 days at room temperature (about 20-25°C. It was found that the hydrogen peroxide concentration after storage was 3.9% in composition A and 2.9% in composition B.

Claims

1. Composition suitable for cleaning, disinfection and/or bleaching characterised in that it comprises, an acidic aqueous solution of hydrogen peroxide, a surfactant, citric acid, and a complexing agent based on phosphonic acid, dipicolinic acid or derivatives thereof.
2. Composition as claimed in claim 1, characterised in that the pH of the aqueous solution is below 4.
3. Composition as claimed in claim 2, characterised in that the pH of the aqueous solution is below 3.
4. Composition as claimed in any one of the claims 1-3, characterised in that the composition does not comprise any substantial amounts of phosphoric acid or phosphates.
5. Composition as claimed in any one of the claims 1-4, characterised in that the composition comprises a phosphonic acid based complexing agent.
6. Composition as claimed in any one of the claims 1-5, characterised in that the composition comprises a complexing agent based on dipicolinic acid or derivatives thereof.
7. Composition as claimed in any one of the claims 1-6, characterised in that the composition comprises as a complexing agent any of picolinic acid, dipicolinic acid, 2,6-pyridine dialdehyde or 2,2-dipyridyl amine.

8. Composition as claimed in any one of the claims 1-7, **characterised** in that the composition comprises a non-ionic surfactant or an amphoteric surfactant or a mixture thereof which is compatible with hydrogen peroxide in acidic solution.

9. Composition as claimed in claim 8, **characterised** in that the composition comprises an amphoteric surfactant satisfying the formula:

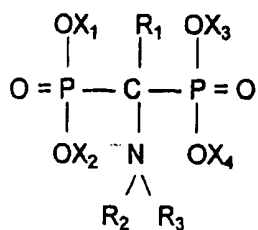


wherein x and y are, independently from each other, from 1 to 5, R' is -COOM₂ or -OH, M₁ and M₂ are, independently from each other, hydrogen, ammonium or an alkali metal, R is a straight or a branched carbon chain having from 1 to 8 carbon atoms or an amide of the formula:



wherein R'' is a straight or a branched carbon chain having from 1 to 8 carbon atoms.

10. Composition as claimed in claim 9, **characterised** in that R' is COOM₂.
11. Composition as claimed in any one of the claims 9-10, **characterised** in that R is a straight or a branched carbon chain.
12. Composition as claimed in any one of the claims 1-11, **characterised** in that the composition comprises a chelating agent selected from biodegradable 1-aminoalkane-1,1-diphosphonic acids, or salts thereof, of the formula:



wherein R₁ is selected from hydrogen, C₁-C₄ alkyl

and phenyl; R₂ and R₃, independently from each other, are selected from hydrogen, C₁-C₂₂ alkyl, C₅-C₆ cycloalkyl, phenyl, C₇-C₁₈ alkylphenyl, C₇-C₁₈ phenylalkyl, a C₁-C₁₀ alkanol radical, a carboxy alkyl radical having up to 10 carbon atoms, wherein R₁ and R₂ together with the nitrogen atom can form a piperidino, pyrrolidino or a morpholino group; and X₁ to X₄, independently from each other, are selected from hydrogen, alkali metal and ammonium.

13. Composition as claimed in claim 12, **characterised** in that the composition comprises a chelating agent selected from morpholinomethane diphosphonic acid, N,N-dimethyl aminodimethyl diphosphonic acid, aminomethyl diphosphonic acid, or salts thereof.

14. Use of a composition according to any of the claims 1-13 for disinfection, bleaching, removal of stains from textiles, or removal of lime deposits.